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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention is excellent in emulsion-polymerization control nature, polymerization time is short, and there is little quantity of residual vinyl acetate, and it excels in the creep resistance characteristic, and, moreover, a formaldehyde content is related with the manufacturing method of few [notably] ethylene-vinyl acetate system resin emulsions.

[0002]

[Description of the Prior Art]Conventionally, the polyvinyl acetate system resin emulsion used as protective colloid polyvinyl alcohol (it may be hereafter written as PVA) For papers, It is widely used in the field of the various binders the various adhesives the object for woodwork, for plastics, etc., the object for impregnated papers, for nonwoven products, etc., admixture, ***** material, a paint, paper coating and textile processing, wallpaper, etc. As a polymerization initiator used at the time of above-mentioned emulsion manufacture, oxidizers, such as hydrogen peroxide, ammonium persulfate, and potassium persulfate, are usually used by a redox system with a reducing agent. When polymerization stability, the water resisting property of an emulsion, etc. are required also in these, hydrogen peroxide is used widely. As a reducing agent of hydrogen peroxide, since the redox reaction with hydrogen peroxide is sharp, the object for ** of sodium formaldehyde sulfoxylate (it is described as a common-name Rongalite and a following Rongalite) is carried out. However, since a Rongalite generates formaldehyde at the time of decomposition, it has the serious problem that formaldehyde is contained in the emulsion obtained. What is called non formalin adhesives are called for strongly, and substitution of said polymerization initiator serves as pressing need from the environmental problem of these days.

[0003]Then, although the technique using a tartrate or a glyoxal bisulfite as a reducing agent which changes to a Rongalite was proposed (JP,2000-212533,A), control of an emulsion

polymerization is difficult only by merely using these reducing agents and oxidizing agent components. It was fatal from a viewpoint of safety to have been an emulsion polymerization under high pressure force in manufacture of an ethylene-vinyl acetate copolymerization emulsion, and for control of a polymerization to have been especially difficult. If it results in a glyoxal bisulfite, although there is no formaldehyde generation, it is not solution of the problem from generating glyoxal which is an aldehyde compound which has the almost same danger at all.

[0004]

[Problem(s) to be Solved by the Invention]This invention is excellent under such circumstances at emulsion-polymerization control nature, Polymerization time is short, and there is little quantity of residual vinyl acetate, and it excels in the creep resistance characteristic, and aims at moreover the content of formaldehyde providing the manufacturing method of few [notably] ethylene-vinyl acetate system resin emulsions.

[0005]

[Means for Solving the Problem]A result of having repeated research wholeheartedly this invention persons developing a manufacturing method of an ethylene-vinyl acetate system resin emulsion which has the aforementioned desirable character, A vinyl alcohol system polymer beyond saponification degree 70 mol % is made into a dispersing agent, A redox system polymerization initiator which consists of hydrogen peroxide, tartaric acid, and/or its metal salt is used, adjusting pH of (1) polymerization system to 3-7, when carrying out the emulsion polymerization of the vinyl acetate to ethylene under application of pressure -- (2) -- an iron compound being added further, and the whole quantity of (3) vinyl acetate being taught in early stages, and to (4) total-monomer 100 weight section, After it will carry out 0.01-0.2 weight-section use of all the hydrogen peroxide and (5) residual vinyl acetate concentration will be 10%, It finds out that a manufacturing method of an ethylene-vinyl acetate system resin emulsion riping by adding 20 to 40% of all the hydrogen peroxide is what satisfies the above-mentioned purpose, and came to complete this invention.

[0006]

[Embodiment of the Invention]The PVA system polymer beyond saponification degree 70 mol % used for the manufacturing method of the ethylene-vinyl acetate system resin emulsion of this invention as a dispersing agent can be obtained by saponifying a vinyl ester system polymer with a conventional method.

[0007]What carried out copolymerization of the copolymerizable ethylenic unsaturated monomer in the range which does not spoil the purpose of this invention may be sufficient as this dispersing agent. As such an ethylenic unsaturated monomer, For example, ethylene, propylene, acrylic acid, methacrylic acid, fumaric acid, (Anhydrous) Maleic acid, itaconic acid (anhydrous), acrylonitrile, a methacrylonitrile, Acrylamide, methacrylamide, trimethyl (3-

acrylamide 3-dimethylpropyl)-ammonium chloride, Acrylamide 2-methylpropanesulfonic acid and its sodium salt, Ethyl-vinyl-ether, butylvinyl ether, N-vinyl-pyrrolidone, VCM/PVC, vinyl bromide, and vinyl fluoridation, a vinylidene chloride, vinylidene fluoride, tetrafluoroethylene, sodium vinylsulfonate, sodium allylsulfonate, etc. are mentioned. Under existence of thiol compounds, such as thiol acetic acid and mercaptopropionic acid, vinyl acetate is polymerized and the terminal modification thing obtained by saponifying it can also be used.

[0008]the saponification degree of the PVA system polymer used as a dispersing agent of the aqueous emulsion of this invention needs to be more than 70 mol % -- more -- desirable -- more than 80 mol % -- it is more than 85 mol % still more preferably. When a saponification degree is less than [70 mol %], since the water solubility which is the original character of a PVA system polymer falls, emulsion-polymerization stability may fall. The degree of polymerization of this PVA system polymer has the preferred range of 100-8000, and 300-3000 are more preferred. When a degree of polymerization is within the limits of this, good protective colloid nature is obtained and it becomes easy [manufacture of a PVA system polymer].

[0009]Although there is no restriction in particular about the amount of the PVA system polymer used as a dispersing agent, it is the range of three to 10 weight section more preferably two to 15 weight section to dispersoid 100 weight section. When the amount of this [used] is within the limits of this, polymerization stability and leaving stability become good.

[0010]In this invention, ethylene and vinyl acetate are mainly used as a monomer. By carrying out emulsification copolymerization of these monomers, the ethylene-vinyl acetate system resin emulsion which makes an ethylene-vinyl acetate system copolymer a dispersoid is obtained.

[0011]In this invention, it is required to teach the whole quantity of the vinyl acetate to be used in early stages. There is the strong point which the ethylene-vinyl acetate system resin emulsion which is excellent in the creep resistance characteristic is obtained, and can shorten polymerization time by teaching the whole quantity of vinyl acetate in early stages.

[0012]Copolymerization of an ethylenic unsaturated monomer and the diene system monomer may be carried out in the range which does not spoil the purpose of this invention. As such a monomer, olefins, such as propylene and isobutylene, Halogenation olefins, such as VCM/PVC and vinyl fluoridation, vinylidenechloride, and a vinylidenefluoride, Acrylic acid, methyl acrylate, ethyl acrylate, butyl acrylate, Acrylic acid and its ester, such as 2-ethylhexyl acrylate, acrylic acid dodecyl, and acrylic acid 2-hydroxyethyl, Methacrylic acid, methyl methacrylate, ethyl methacrylate, butyl methacrylate, Methacrylic acid and its ester, such as 2-ethylhexyl methacrylate, methacrylic acid dodecyl, and methacrylic acid 2-hydroxyethyl, To acrylic acid dimethylaminoethyl, dimethylaminoethyl methacrylate and the fourth class ghosts of these, and a pan. Acrylamide, methacrylamide, N-methylolacrylamide, Acrylamide system

monomers, such as N,N-dimethylacrylamide and acrylamide 2-methylpropanesulfonic acid and its sodium salt, Butadiene, such as styrene monomers, such as styrene, alpha-methylstyrene, p-styrene sulfonic acid and sodium, and potassium salt, and other N-vinyl pyrrolidone, isoprene, Polyfunctional monomers, such as diene system monomers, such as chloroprene, and also triaryl cyanurate, triallyl isocyanurate, and diallyl phthalate, are mentioned.

[0013]In the manufacturing method of this invention, the redox system polymerization initiator which consists of hydrogen peroxide, tartaric acid, and/or its metal salt is used as a polymerization initiator. Although there are dextro-rotatory L (+) tartaric acid, levo-rotatory D (-) tartaric acid, and DL tartaric acid that is the racemic compounds of these antipodes as tartaric acid and it is not restricted in particular, when L (+) tartaric acid is used also in these, emulsion-polymerization control nature is notably good, and is used preferably. Although it is also possible to use metal salt of tartaric acid and a metaled kind in particular is not restricted, the sodium tartrate is used suitably. L (+) sodium tartrate is used preferably especially. When L (+) sodium tartrate is used, it not only excels in polymerization control nature, but the pH adjustment at the time of the emulsion polymerization mentioned later becomes easy.

[0014]In this invention, the amount of the hydrogen peroxide used needs to be 0.01 to 0.2 weight section to the total monomer to be used, and is 0.03 to 0.1 weight section more preferably 0.02 to 0.15 weight section. Since polymerization reaction speed falls notably when there is less amount used than 0.01 weight sections, it is unsuitable, and since control of a polymerization reaction becomes difficult in exceeding 0.2 weight section, it is unsuitable.

[0015]Although the amount in particular of tartaric acid and/or its metal salt used is not restricted, it is 0.2-1 mol to 1 mol of hydrogen peroxide, and is 0.3-0.8 mol still more preferably 0.25-0.9 mol preferably. When the using rate of tartaric acid and/or its metal salt is less than 0.2 mol, the control nature of a polymerization reaction falls, and when exceeding 1 mol, the pH adjustment of an emulsion-polymerization system may become difficult.

[0016]It is important to prepare pH of an emulsion-polymerization system to 3-7 in the manufacturing method of this invention, and adjusting to 4-6.5 is preferred. When pH of an emulsion-polymerization system is lower than three, since redox reaction speed with hydrogen peroxide, tartaric acid, and/or its metal salt falls notably and control of a polymerization becomes difficult, it is unsuitable. When pH of an emulsion-polymerization system is higher than seven, a possibility that hydrolysis of vinyl acetate may start into an emulsion polymerization arises, and it is unsuitable. The adjustment method in particular of pH of an emulsion-polymerization system is not restricted, but although it is possible to use arbitrary buffers, sodium acetate, acetic acid / sodium acetate system, sodium hydroxide, sodium carbonate, etc. are usually used preferably. It is also possible to carry out pH preparation, without using a buffer, when using metal salt of the tartaric acid carried out in the first half, for example, the sodium tartrate. It is important that pH of an emulsion-polymerization system

means pH from the early stages of a polymerization to the end of a polymerization in this invention, and pH is in 3-7 in this invention at which time of a polymerization system.

[0017]It is important from making control nature of an emulsion polymerization into the more outstanding thing to add an iron compound in an emulsion-polymerization system in the manufacturing method of this invention. Although not restricted especially as an iron compound, at least one sort of iron compounds chosen from ferrous chloride, ferrous sulfate, ferric chloride, the second iron of nitric acid, and ferric sulfate are used preferably, and ferrous chloride and ferrous sulfate are used especially preferably.

[0018]Although the amount in particular of the iron compound used is not restricted, 1-50 ppm is 5-30 ppm more preferably to the total monomer which carries out normal use. When the amount of the iron compound used is within the limits of this, control of a polymerization is good, and it is hard to color when the obtained emulsion is coat-ized. Although the addition method in particular of an iron compound is not restricted, either, the method of adding the whole quantity in early stages of an emulsion polymerization is usually preferred.

[0019]In this invention, after residual vinyl acetate concentration will be 10% (it may be hereafter written as the second half of a polymerization), it is important to ripe by adding 20 to 40% of all the hydrogen peroxide used for an emulsion polymerization. When the hydrogen peroxide used in the second half of a polymerization is less than 20%, there is a possibility that the amount of residual vinyl acetate monomers after the end of a polymerization may increase, and it is unsuitable. When the hydrogen peroxide used in the second half of a polymerization surpasses 40%, time until residual vinyl acetate concentration will be 10% (it may be hereafter written as the first half of a polymerization) becomes long, there is a possibility that productivity may get worse, and it is unsuitable. In the first half of a polymerization, under application of pressure, although an emulsion polymerization is suitably performed under the application of pressure of 30 - 70 kg/cm², in the second half of a polymerization -- the pressure in early stages of a polymerization -- 5 - 35 kg/cm² -- the bottom of a low pressure -- suitable -- 10 - 30 kg/cm² -- it is preferred from the ability to lessen quantity of residual vinyl acetate to carry out under a low pressure, to emit some ethylene and to ripe. The polymerization time in early stages of a polymerization is chosen from the range of 3 to 7 hours. the maturing time in the second half of a polymerization -- the range of 0.3 to 3 hours -- it is suitably chosen out of the range of 0.5 to 2 hours. according to this invention -- polymerization time (total time in the first half of a polymerization, and the second half of a polymerization) -- less than seven between and less than 6 more hours -- a polymerization can be finished comparatively in a short time.

[0020]It is important for the ethylene-vinyl-acetate-resin system emulsion obtained by the manufacturing method of this invention that the formaldehyde concentration contained in an emulsion is less than 5 ppm. The numerical value which performed measurement of the

formaldehyde concentration in an emulsion using the gas detector is said here, and a measuring method is explained in full detail in the example shown below. When the formaldehyde concentration contained in an emulsion is not less than 5 ppm, it cannot be called what is called a non formalin emulsion. It is more preferred for formaldehyde concentration that it is less than 3 ppm, and it is more preferred that it is less than 1 more ppm.

[0021]Alkali, such as ammonia and caustic alkali of sodium, can adjust the ethylene-vinyl-acetate-resin system emulsion obtained with the manufacturing method of this invention to desired pH after an emulsion polymerization. Although the emulsion obtained by the above-mentioned method can be used for it as it is, if the ethylene-vinyl-acetate-resin system emulsion obtained with the manufacturing method of this invention has necessity, it is a range which does not spoil the effect of this invention, and various publicly known emulsions can be conventionally added and used for it. Although the above-mentioned PVA system polymer beyond saponification degree 70 mol % is used as a dispersing agent used for this invention, anionic [publicly known], a nonionic or cationic surface-active agent, hydroxyethyl cellulose, etc. can also be conventionally used together if needed.

[0022]The ethylene-vinyl-acetate-resin system emulsion obtained by the manufacturing method of this invention, or [hardly containing formaldehyde in an emulsion] -- or, since it does not contain at all and excels in creep resistance, It is preferably used as the base emulsion for wallpaper, building materials especially the adhesives for inner packages, a paint, etc., It is suitably used also in fields, such as adhesives for woodwork, such as adhesives for paper coatings, such as papers a paper tube, bag manufacture, interleaving paper, for corrugated fiberboards, etc., and pulp, and general woodwork, and the adhesives for various plastics, the object for impregnated papers, a binder for nonwoven products, admixture, ***** material, paper coating, and textile processing.

[0023]

[Example]Next, an example and a comparative example explain this invention still in detail. A weight reference is meant unless it refuses especially a "part" and "%" in the following examples and comparative examples. The following way estimated emulsion physical properties, such as a formaldehyde content etc. of the obtained emulsion, the control nature of the emulsion polymerization, etc.

[0024](Valuation method)

(1) 0.1g of emulsions were extracted to the formaldehyde content glass vial of 10 ml, and after carrying out 40 **x1hr warming, it measured with the gas detector (No.171SB: the product made from the Mitsuaki science, 100-ml suction).

(2) Control nature of an emulsion polymerization -- When addition of whether generation of heat by polymerization stops promptly when addition of hydrogen peroxide is stopped, and

hydrogen peroxide was started, it observed whether a polymerization would advance promptly and generation of heat would start, and the following standard estimated.

O : it is fitness to a control nature emergency. -- When generation of heat by polymerization stops promptly when addition of hydrogen peroxide is stopped, and addition of hydrogen peroxide is started, a polymerization advances promptly and generation of heat starts.

O : control nature fitness -- When addition of hydrogen peroxide is stopped, generation of heat by polymerization stops promptly, but when addition of hydrogen peroxide is started, a rate of polymerization becomes slow somewhat and generation of heat becomes small.

** : Control nature and ** are poor. -- When addition of hydrogen peroxide is stopped, it is hard to stop generation of heat by polymerization, or when addition of hydrogen peroxide is started, a polymerization does not advance promptly, but it generates heat, and is a difficulty stake.

x: Control is impossible. -- It does not generate heat, when generation of heat by polymerization does not stop promptly when addition of hydrogen peroxide is stopped, or addition of hydrogen peroxide is started, and a polymerization does not advance.

(3) Polymerization time -- Total time in the first half of a polymerization, and the second half of a polymerization.

(4) Residual vinyl acetate (VAc) -- The amount of residual vinyl acetate monomers after the end of an emulsion polymerization was measured by JIS K-6828.

(5) Creep resistance physical properties -- It examined based on JIS K-6859. That is, after 100-g/m^2 -applying the emulsion obtained by the plywood, the plasticized-polyvinyl-chloride film was pasted together (adhesion area 2 of 1 cm), and it dried at 20 **. Then, 500 g of load was applied to the end of a vinyl chloride film, and the following standard estimated.

O Exfoliate an adhesion state maintenance and less than [x1 week] one week or more. [0025]
An example 1 nitrogen entrainment mouth, a thermometer, and an agitator to resisting pressure the autoclave of 50 l. which it had PVA-1{degree-of-polymerization 1700 and saponification degree [of 88 mol] %, 1061 g, the ion exchange water 19440g, the L (+) tartaric acid 8.3g, the sodium acetate 10g, and the ferrous chloride 0.4g were prepared, PVA-217 by Kuraray Co., Ltd.} was thoroughly dissolved at 95 **, it cooled at 60 ** after that, and the nitrogen purge was performed. It was pH=5.5 when the pH of solution was checked. Next, after teaching 22360 g of vinyl acetate, ethylene was pressurized to 45 kg/cm^2 . The hydrogen peroxide (HPO) solution 1000g was pressed fit over 5 hours 0.4%, and the emulsion polymerization was performed. In the place where residual vinyl acetate concentration became 10%, some ethylene was emitted, it was considered as ethylene pressure 20 kg/cm^2 , the hydrogen-peroxide-solution solution 50g was pressed fit 3%, it riped for 1 hour, and the polymerization was completed. After cooling, when pH was checked, it was pH=4.6. 230g of sodium hydroxide solution was added 10%, pH of the emulsion was adjusted to 5.5, and it

filtered using the wire gauze made from stainless steel of 60 meshes. As a result, 54.5% of solids concentration and the ethylene-vinylacetate copolymer emulsion (Em-1) of 18 % of the weight of ethylene contents were obtained. The above-mentioned method estimated. A result is shown in Table 1.

[0026]In comparative example 1 Example 1, the Rongalite was used instead of L (+) tartaric acid, and also the emulsion (Em-2) was obtained like Example 1. The evaluation result of this emulsion is collectively shown in Table 1.

[0027]Sodium acetate was not used in comparative example 2 Example 1, and also the emulsion (Em-3) was obtained like Example 1. The evaluation result of this emulsion is collectively shown in Table 1.

[0028]Ferrous chloride was not used in comparative example 3 Example 3, and also the emulsion (Em-4) was obtained like Example 1. The evaluation result of this emulsion is collectively shown in Table 1.

[0029]PVA-1 to resisting pressure the autoclave of 50 l. provided with the comparative example 4 nitrogen entrainment mouth, the thermometer, and the agitator 1061 g, The ion exchange water 19440g, the L (+) tartaric acid 8.3g, the sodium acetate 10g, and the ferrous chloride 0.4g were prepared, and it dissolved thoroughly at 95 **, and cooled at 60 ** after that, and the nitrogen purge was performed. It was pH=5.5 when the pH of solution was checked. Next, after teaching 2236 g of vinyl acetate, ethylene was pressurized to 45 kg/cm^2 . After pressing the hydrogen-peroxide-solution solution 24g fit 5% and performing an initial polymerization, consecutive addition of 20124g of vinyl acetate and the 0.4% hydrogen peroxide 700g was carried out, and the emulsion polymerization was performed. In the place where residual vinyl acetate concentration became 10%, some ethylene was emitted, it was considered as ethylene pressure 20 kg/cm^2 , the hydrogen-peroxide-solution solution 50g was pressed fit 3%, it riped for 1 hour, and the polymerization was completed. After cooling, when pH was checked, it was pH=4.5. 230g of sodium hydroxide solution was added 10%, pH of the emulsion was adjusted to 5.5, and it filtered using the wire gauze made from stainless steel of 60 meshes. As a result, 54.6% of solids concentration and the ethylene-vinylacetate copolymer emulsion (Em-5) of 19 % of the weight of ethylene contents were obtained. The above-mentioned method estimated. A result is collectively shown in Table 1.

[0030]PVA-1 to resisting pressure the autoclave of 50 l. provided with the comparative example 5 nitrogen entrainment mouth, the thermometer, and the agitator 1061 g, The ion exchange water 19440g, the L (+) tartaric acid 8.3g, the sodium acetate 10g, and the ferrous chloride 0.4g were prepared, and it dissolved thoroughly at 95 **, and cooled at 60 ** after that, and the nitrogen purge was performed. It was pH=5.4 when the pH of solution was checked. Next, after teaching 22360 g of vinyl acetate, ethylene was pressurized to 45 kg/cm^2 . The

hydrogen-peroxide-solution solution 1000g was pressed fit over 5 hours 4.8%, and the emulsion polymerization was performed. In the place where residual vinyl acetate concentration became 10%, some ethylene was emitted, it was considered as ethylene pressure 20 kg/cm^2 , the hydrogen-peroxide-solution solution 360g was pressed fit 5%, it riped for 1 hour, and the polymerization was completed. After cooling, when pH was checked, it was pH=5. 230g of sodium hydroxide solution was added 10%, pH of the emulsion was adjusted to 5.5, and it filtered using the wire gauze made from stainless steel of 60 meshes. As a result, 54.5% of solids concentration and the ethylene-vinylacetate copolymer emulsion (Em-6) of 18 % of the weight of ethylene contents were obtained. The above-mentioned method estimated. A result is collectively shown in Table 1.

[0031]PVA-1 to resisting pressure the autoclave of 50 l. provided with the comparative example 6 nitrogen entrainment mouth, the thermometer, and the agitator 1061 g, The ion exchange water 19440g, the L (+) tartaric acid 8.3g, the sodium acetate 10g, and the ferrous chloride 0.4g were prepared, and it dissolved thoroughly at 95 **, and cooled at 60 ** after that, and the nitrogen purge was performed. It was pH=5.5 when the pH of solution was checked.

Next, after teaching 22360 g of vinyl acetate, ethylene was pressurized to 45 kg/cm^2 . The hydrogen-peroxide-solution solution 500g was pressed fit over 5 hours 0.4%, and the emulsion polymerization was performed. In the place where residual vinyl acetate concentration became 10%, some ethylene was emitted, it was considered as ethylene pressure 20 kg/cm^2 , the hydrogen-peroxide-solution solution 117g was pressed fit 3%, it riped for 1 hour, and the polymerization was completed. After cooling, when pH was checked, it was pH=4.5. 230g of sodium hydroxide solution was added 10%, pH of the emulsion was adjusted to 5.5, and it filtered using the wire gauze made from stainless steel of 60 meshes. As a result, 54.5% of solids concentration and the ethylene-vinylacetate copolymer emulsion (Em-7) of 18 % of the weight of ethylene contents were obtained. The above-mentioned method estimated. A result is collectively shown in Table 1.

[0032]PVA-2 [1592g] {degree-of-polymerization 1700 and PVA-617 by saponification degree % and Kuraray Co., Ltd. of 95 mol} was used instead of using PVA-1 [1061g] in example 2 Example 1, and also the emulsion (Em-8) was obtained like Example 1. The evaluation result of this emulsion is collectively shown in Table 1.

[0033]in example 3 Example 1 -- instead of [of L (+) tartaric acid] -- L (+) sodium tartrate -- this mol -- it used and also the emulsion (Em-9) was obtained like Example 1. The evaluation result of this emulsion is collectively shown in Table 1.

[0034]

[Table 1]

	PVA	HPO (総量)	HPO添加比率		還元剤	鉄化合物		緩衝剤	pH		ホルム アルデヒド (ppm)	乳化重合の コントロール性	重合 時間	残 VAc (%)	耐 クリープ
			重合 前期 (%)	重合 後期 (%)		(モル /HPO)	(ppm)		初期	最後					
実施例1	PVA-1	0.02	72.7	27.3	L(+)-酒石酸	0.49	あり	酢酸ナトリウム	5.5	4.6	0	◎	6	0.3	○
比較例1	PVA-1	0.02	72.7	27.3	ロザリット	0.49	あり	酢酸ナトリウム	4.0	3.7	35以上	◎	6	0.4	○
比較例2	PVA-1	0.02	72.7	27.3	L(+)-酒石酸	0.49	あり	なし	3.4	2.4	0	△	8	1.2	○
比較例3	PVA-1	0.02	72.7	27.3	L(+)-酒石酸	0.49	なし	酢酸ナトリウム	5.5	4.1	0	△	8.5	1.1	○
比較例4	PVA-1	0.02	72.7	27.3	L(+)-酒石酸	0.49	あり	酢酸ナトリウム	5.5	4.5	0	◎	7.5	0.3	×
比較例5	PVA-1	0.24	72.7	27.3	L(+)-酒石酸	0.49	あり	酢酸ナトリウム	5.4	5	0	△	5	0.3	○
比較例6	PVA-1	0.02	36.4	63.6	L(+)-酒石酸	0.49	あり	酢酸ナトリウム	5.5	4.5	0	○	9	0.4	○
実施例2	PVA-2	0.02	72.7	27.3	L(+)-酒石酸	0.49	あり	酢酸ナトリウム	5.6	4.7	0	◎	6.5	0.3	○
実施例3	PVA-1	0.02	72.7	27.3	L(+)-酒石酸 ナトリウム	0.49	あり	酢酸ナトリウム	5.5	4.5	0	◎	6	0.3	○

HPO:全単量体100重量部に対する重量部

HPO比率:重合前期及び重合後期に使用したHPOの比率

還元剤:HPOに対するモル比

[0035]

[Effect of the Invention]The manufacturing method of this invention is excellent in the control nature of an emulsion polymerization, and its polymerization time is short, The ethylene-vinyl-

acetate-resin system emulsion from which there is little quantity of residual vinyl acetate, and it is obtained by the manufacturing method of this invention, or [hardly containing formaldehyde] -- or, since it does not contain at all and excels in creep resistance, It is preferably used as the base emulsion for wallpaper, building materials especially the adhesives for inner packages, a paint, etc., It is suitably used also in fields, such as adhesives for woodwork, such as adhesives for paper coatings, such as papers a paper tube, bag manufacture, interleaving paper, for corrugated fiberboards, etc., and pulp, and general woodwork, and the adhesives for various plastics, the object for impregnated papers, a binder for nonwoven products, admixture, ***** material, paper coating, and textile processing.

[Translation done.]